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Recovery of *n*-butanol using ionic liquid-based pervaporation membranes

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ABSTRACT

Biobutanol (*n*-butanol) offers the possibility of expanding the production of bulk chemicals and fuels based on renewable resources. A drawback in the microbial production of *n*-butanol is the energy-intensive product recovery process, making biobutanol expensive. One method for overcoming this limitation is the application of supported ionic liquid membranes (SILMs) for continuous product removal.

In this work, the pervaporation performance of SILMs with tetracyanoborate and tris(pentafluoroethyl)trifluorophosphate ionic liquids (ILs) was investigated. Pervaporation was carried out at 37 °C using binary mixtures of *n*-butanol and water with *n*-butanol concentrations lower than 5 wt.%. Two concepts for immobilisation of ILs were tested using nylon or polypropylene as support material. ILs were immobilised by inclusion between silicone layers or by dissolution in poly(ether block amide). It was observed that a higher affinity of the IL for *n*-butanol increases the permeability of the membrane for more than three times, whereas no changes in the selectivity occurred. Furthermore it was shown, that fluxes increased with an increasing IL content in the membrane. The maximum permeate flux achieved was 560 g/(m^2 h), and the highest concentrations of *n*-butanol in the permeate was found to be 55 wt.%. In future thickness of SILMs needs to be reduced to make these membranes competitive with respect to conventional pervaporation membranes.

1. Introduction

The shrinking of fossil fuel resources and growing environmental awareness have driven the search for new routes for the synthesis of fuels from renewable resources. One example is the microbial production of biobutanol (*n*-butanol). Drawbacks of this process are the high toxicity of *n*-butanol to the production organisms and the resulting low concentrations of *n*-butanol in the fermentation broth, limiting the productivity of the process [1,2]. In China several large-scale fermentation processes have been established for the production of *n*-butanol since 2007. Distillation processes are currently used as "end-of-pipe" technologies for the recovery of *n*-butanol [3]. Unfortunately, these processes generate large wastewater streams and require high energy consumption, which can be reduced by the continuous separation of *n*-butanol from the fermentation broth. In particular, the *in situ* extraction of *n*-butanol and separation via pervaporation were found to be promising [4,5].

Oleyl alcohol has been considered in the past as a potential extractant of *n*-butanol from the fermentation broth [6,7]. In comparison to oleyl alcohol, novel extraction solvents such as ionic liquids (ILs) show similar distribution coefficients and selectivities [8], and the ILs' properties, such as the melting point, viscosity and density, can be adjusted based on the process requirements. These properties can be changed, for example, by combining different cations and anions or by the introduction of functional groups into the ions [9]. In particular, ILs containing tetracyanoborate anions such as 1-decyl-3-methylimidazolium tetracyanoborate and trihexyltetradecylphosphonium tetracyanoborate are reported to be suitable for the extraction of *n*-butanol [10]. However, extraction with ILs might have some shortcomings, such as toxicity issues [11] or a large demand for ILs for extraction. One possibility to overcome these potential limitations is the recovery of *n*-butanol by pervaporation through membranes in which ILs are immobilised in pores. Such supported ionic liquid membranes (SILMs) are often investigated for use in gas permeation processes [12,13]. The negligible vapour pressure of ILs is a favourable property to prevent leaching in gas permeation. Additionally, the separation characteristics of the membranes can be tuned by varying the type and quantity of the immobilised IL. Substituting IL-based extraction with a pervaporation with SILMs reduces the IL demand for broth purification and avoids direct contact between the production organisms and the IL, as long as no leaching of the IL occurs. In this case the potential toxicity of ILs becomes less important. Hence, permanent IL immobilisation is crucial for the technical application of SILMs.

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The issue of immobilisation has already been addressed in catalysis research, in which ILs are used as supported ionic liquid phases (SILPs) [14], in investigations of polymer electrolytes used in fuel cells [15] and in the production of solar cells [16]. An overview of some methods for utilising ILs as an active separation layer in membranes is given in Fig. 1. The first approach is the linking of polymerisable groups to the IL molecules and the direct cross-linking of the ILs by covalent bonding (a). In this case, the IL's properties are changed, and the resulting SILM exhibits a permeation behaviour that is different from that of neat ILs, as shown by the Noble research group [12]. Thus, the choice of a suitable IL based on extraction and the transfer of the IL properties to SILMs may not always be appropriate. In another approach, anions or cations of ILs might be immobilised in ion exchange membranes (b). Next to these concepts for immobilisation, ILs can be solidified by the use of gelling agents [17,18]. Gelators allow IL contents higher than 90 wt.% in gels, but low chemical and mechanical stability limit their suitability for pervaporation (c). In related systems, ILs are often solidified by dissolving these liquids in a polymer (d). In the literature, a wide range of so-called host polymers, such as poly(vinylidenefluoride)-hexafluoropropylene (PVDF-HFP), polyvinyl alcohol (PVA), polyvinyl chloride (PVC), poly(dimethyl siloxane) (PDMS), poly(ether block amide) (PEBA) and others, has been reported [19–23].

The easiest way to prevent leaching of ILs into the liquid feed during pervaporation is probably the inclusion of ILs in membranes with an additional coating with a polymer such as PDMS or silicone (e). These polymers are usually suitable for the pervaporative separation of organic compounds from water [24]. It seems obvious that an additional IL layer added to the PDMS membrane or the combination of IL and PDMS layers will result in a higher mass transfer resistance of the whole membrane. However, Yu et al. observed that this combination results in higher fluxes of acetic acid compared to neat PDMS membranes [25]. A similar approach combining PDMS layers with ILs was also used by Izák et al., who immobilised tetrapropylammonium tetracyanoborate in a ceramic nanofiltration membrane [26]. Izák et al. observed that without immobilisation, the IL was flushed out of the pores by the feed solution, although the operating temperature was far below the melting point of the IL. To overcome this problem, a ceramic membrane impregnated with IL was coated with a layer of PDMS. In the separation of 1,3-propanediol from an aqueous mixture, permeate concentrations of approximately 60 wt.% and permeate fluxes smaller than 10 g/(m^2 h) were obtained using this so-called multi-phase membrane [27].

In another work by Izák et al., a different approach was used to immobilise ILs in membranes. Two ILs were included into silicone as host polymer [22]. The maximum total permeate flux achieved by the resulting membrane containing 50 wt.% of tetrapropylammonium tetracyanoborate was 90 g/(m^2 h) at a concentration of 18 wt.% *n*-butanol in the permeate. In general, the addition of an IL to silicone decreased the permeate flux slightly but increased the permeate concentration of *n*-butanol. In a similar work, Kohoutová et al. examined the influence of the IL content on the permeation properties when the IL was included in a silicone matrix [28]. The IL content was varied between 0 and 30 wt.%, resulting in permeate fluxes of approximately 55 g/(m^2 h), which were nearly independent of the IL content. In contrast to the permeate flux, the concentration of *n*-butanol in the permeate increased by 50% with an increasing IL content in the membrane. In 2011, Matsumoto et al. described polymer inclusion membranes containing up to 70 wt.% of different ILs in PVC [21]. In the pervaporation of *n*-butanol and isopropyl alcohol, the inclusion of ILs resulted in *n*-butanol fluxes of 27 g/(m^2 h) with permeate concentrations of *n*-butanol lower than 10 wt.%. Unfortunately, a direct comparison of different SILMs described in literature is difficult because primary factors influencing pervaporation, e.g., feed concentrations, permeate pressures, temperatures and membrane thicknesses, vary.

Future promising applications of SILMs in technical separation processes can only be possible if SILMs are able to compete with conventional membranes in terms of stability, flux and separation efficiency. An overview of membranes used for the pervaporation of *n*-butanol can be found in papers of Oudshoorn et al. and Liu et al. [24,29]. According to Oudshoorn et al., it is reasonable to assume a standard *n*-butanol flux of 20–100 g/(m^2 h) when handling fermentation broth. For model solutions consisting of only *n*-butanol and water, higher *n*-butanol fluxes have been reported [24]. Generally, fluxes of SILMs are often lower than fluxes through polymeric, ceramic and several types of composite membranes.

To make SILMs competitive, the permeate fluxes have to be increased. This increase can be achieved in different ways. The easiest way is to reduce the thickness of the active separation layer. Unfortunately, reducing the thickness can result in lower selectivities at a certain value. The use of additional coatings should be avoided or minimised. The selection of more suitable ILs might result in increased fluxes. Furthermore, a high content of IL in the membrane could result in higher fluxes [21] and/or selectivities [28].

In this work, two different concepts for the pervaporation of *n*-butanol out of aqueous solutions were investigated, both of which involved membranes with immobilised ILs. The influence of different ILs on the permeation properties of the membranes was tested using 1-decyl-3-methylimidazolium tetracyanoborate ($Im_{10,1}$ tcb), trihexyltetradecylphosphonium tetracyanoborate ($P_{6,6,6,14}$ tcb) and 1-decyl 3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ($Im_{10,1}$ fap) (Fig. 2). For this purpose, the

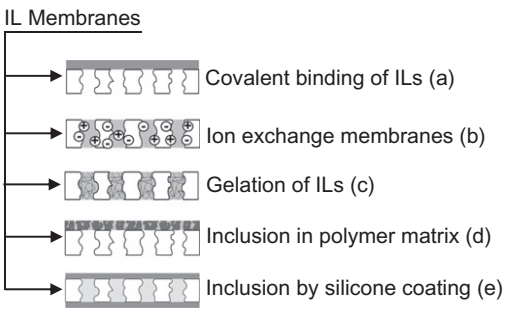

Fig. 1. Different approaches for utilising ILs as membrane material.

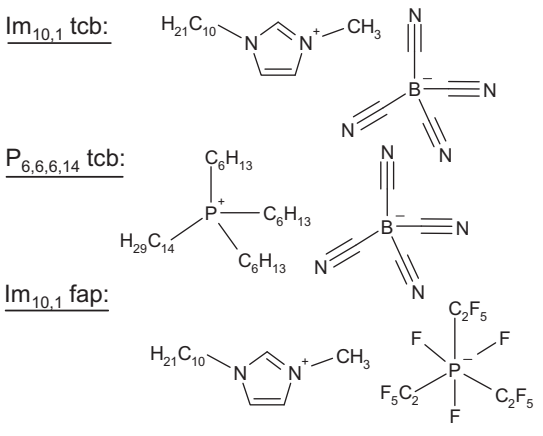

Fig. 2. ILs used for membrane preparation.

ILs were incorporated in a porous membrane using two polymer layers of PDMS, as described by Izák et al. [27], to prevent possibly leaching of the ILs. It was also determined if inclusion of the ILs in a polymer matrix yields functional membranes suitable for the pervaporation of *n*-butanol. In this case, the use of additional polymer layers and thus the corresponding additional mass transfer resistances can be avoided. PEBA was chosen as the host polymer because of its favourable pervaporation characteristics for hydrophobic pervaporation and because silicone was not suitable for the dissolution of $Im_{10,1}$ tcb.

2. Experimental

2.1. Materials

Polypropylene (PP) membranes (Accurel PP, Membrana GmbH, 0.2 μm pore size) and nylon membranes (Ultipor NTG, Pall GmbH, 0.1 μm pore size) were used as porous support materials for membrane preparation. Coating of the membranes was performed using a one-component, fast-cure silicone (Momentive Performance Materials, TSE 399C). Acetic acid (96%), *n*-hexane (96%) and acetonitrile (99.9%) were purchased from VWR International GmbH, Darmstadt. *n*-Butanol (99.9%) was obtained from Sigma Aldrich, Germany. The ILs $Im_{10,1}$ tcb, $P_{6,6,6,14}$ tcb and $Im_{10,1}$ fap were kindly supplied by Merck KGaA. Poly(ether block amide) PEBAX® 2533 was purchased from PRO-plast Kunststoff GmbH, Darmstadt.

2.2. Membrane preparation

2.2.1. Inclusion of ILs using a double-sided silicone coating

The inclusion of the ILs in a porous membrane using a double-sided silicone coating was carried out in two steps. First, the porous support membrane was impregnated with $Im_{10,1}$ tcb, $P_{6,6,6,14}$ tcb or $Im_{10,1}$ fap by submerging the porous membrane into the IL in a petri dish, placing it in a desiccator and applying a vacuum of 10 mbar to the submerged membrane. About 20 min later the desiccator was aerated and vacuum was applied again. This procedure was repeated for three times at room temperature to ensure that all pores of the support membrane are filled by the IL. After removing the membrane from the petri dish, excess IL on the surface of the membrane was carefully wiped off using a soft cloth. The silicone coating solutions were prepared in closed glass vials at room temperature by mixing 10–80 wt.% hexane and silicone at room temperature. Fifteen grams of a mixture were poured into a petri dish; the impregnated membranes were dipped into the silicone solutions containing different amounts of hexane and hung up to allow the excess silicone to drip overnight. Then the membranes were placed in a fume hood for more than 24 h for the completely evaporation of hexane and to ensure the completely curing of the silicone. For preparation of the coated IL membranes, nylon membranes were used as a support. Due to hydrophilic interactions between the IL and the nylon support, the extrusion of the IL from the pores by the silicone–hexane mixture was prevented.

Addition of the hexane to the silicone was used to minimise the thickness of the silicone layers. The viscosity of the pure silicone was 1950 mPa s (25 °C). Silicone was mixed with hexane in ratios of 6:4, 4:6 and 2:8 [wt./wt.], leading to lower viscosities and therefore to thinner residual silicone layers. Fifteen grams of the silicone–hexane mixture containing 40, 60 or 80 wt.% of hexane were poured into a petri dish directly after mixing the two components. PP membranes were dip-coated and after evaporation of hexane and curing of the silicone, the thickness of the silicone layer was determined by scanning electron microscopy (SEM, Hitachi H-S4500 FEG). Average thicknesses of the membranes were 51, 17 and 5 μm.

Both the coated membranes containing ILs as well as the neat silicone layers on PP were tested in *n*-butanol pervaporation experiments in a laboratory pervaporation plant as described in Section 2.3.

2.2.2. Dissolution of IL in a PEBA matrix

Because $Im_{10,1}$ tcb exhibited the best pervaporation performance when immobilised by a silicone coating, this IL was used for further investigations. PEBA was dissolved in acetic acid at a ratio of 1:4 [wt./wt.]. The components were mixed in tightly closed glass vials and placed in an oven at 80 °C for 24 h. $Im_{10,1}$ tcb was added to the mixture at mass ratios of 10:1, 10:3, 2:1 and 1:1 [wt./wt.] relative to PEBA. After pouring 15 g of the mixture into a preheated petri dish (80 °C), the PP membranes were dip-coated with the PEBA-acetic acid-IL solution. The membranes were hung up to allow the excess PEBA-IL-acetic acid mixture to drip off. In order to evaporate residual acetic acid, the membranes were placed in a desiccator at room temperature and exposed to vacuum (<10 mbar) overnight. After evaporation of the acetic acid, neat PEBA and PEBA-IL membranes were tested in a laboratory pervaporation plant. The mass of IL immobilised in the PEBA-IL layer can be calculated, based on the weight of the coating and the IL content.

2.3. Pervaporation experiments

Pervaporation experiments were performed in a laboratory-scale pervaporation plant (Fig. 3) described elsewhere [30]. Circular samples with a diameter of 13 cm were cut from the membranes produced according to the procedure described above. These samples were placed in a flat circular membrane module (Helmholz-Zentrum Geesthacht) with an effective membrane area A_M of 104 cm^2. The temperature of the feed solution (volume: 1.5 L) containing 1–5 wt.% of *n*-butanol was kept constant at 37 °C using an oil bath. The feed flow rate was 35 L/h, and the retentate was recirculated to the feed vessel. Because the permeate volume is negligible compared with the total feed volume, a quasi-steady state in the experiments can be assumed. Feed samples (4 mL) were taken at the beginning and at the end of each experiment. The permeate pressure was adjusted to 10 mbar by a vacuum pump. The permeate was collected in a cooling trap at temperatures lower than −65 °C, cooled using a mixture of isopropanol and dry ice. The total permeate flux J_{total} was determined using Eq. (1). The mass fraction of *n*-butanol $w_{B,P}$ describes the ratio of the *n*-butanol flux J_B relative to the total flux J_{total} through the membrane (Eq. (2)).

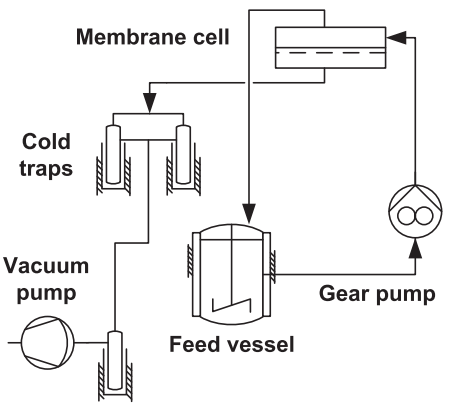

Fig. 3. Scheme of the pervaporation laboratory plant.

$$J_{total} = m_P/(A_M \cdot t) \quad (1)$$

$$w_{B,P} = J_B/J_{total} \quad (2)$$

The mass of permeate m_P collected in a certain time t was determined by weighing the cooling traps before and after one experiment. The concentrations of *n*-butanol in the feed and in the permeate $w_{B,F}$ and $w_{B,P}$ were analysed by gas chromatography (Shimadzu 14a) using flame ionisation detection at 250 °C for analysis of a sample volume of 5 μL. The chromatograph was equipped with a capillary column (FS-Innopeg-FFAP). Helium was used as mobile phase and acetonitrile as internal standard with *n*-butanol to acetonitrile ratios of 0.01 to 3.55 [g/g]. Furthermore, acetonitrile served as a solubiliser to convert the two-phase permeate into a one-phase system for analysis. To minimise analytical errors all concentrations were determined threefold.

3. Results and discussion

3.1. Inclusion of ILs using a double-sided silicone coating

Preliminary tests were performed to minimise the mass transfer resistance of the silicone layer by producing a thin but stable silicone coating for immobilisation of the ILs. The thickness of the coatings was adjusted by adding different amounts of hexane to the silicone. For high silicone-to-hexane ratios, the silicone layers were too thick; thus, no influence of the IL on the permeation properties could be identified. Using a silicone-to-hexane ratio of 9:1 [wt./wt.], all membranes exhibited similar permeate fluxes, which were lower than 50 g/(m^2 h), and similar permeate mass fractions, which were lower than 80 wt.% of *n*-butanol, independent of the IL immobilised in the membrane. The influence of the ILs on the permeation properties can only be observed when the silicone layer is sufficiently thin. The optimal silicone-to-hexane ratio was found to be 1:4 [wt./wt.], yielding a coating thickness of approximately 5 μm, as shown in Fig. 4a. For lower ratios, no stable coating could be obtained.

Fig. 5a and b show the pervaporation performance of IL membranes coated with the 5-μm-thick silicone layer. During all experiments, the weight of the membrane did not decrease, indicating that the ILs were stably incorporated in the porous support. Fig. 5a shows the dependence of the total permeate flux on the feed concentration of *n*-butanol. The type of IL immobilised in the different membranes influences the permeate fluxes. Among the SILMs, the highest flux of approximately 220 g/(m^2 h) was obtained for the membranes containing $Im_{10,1}$ tcb. This flux is two times greater than that of the membranes containing $P_{6,6,6,14}$ tcb and more than three times greater than that of the $Im_{10,1}$ fap membrane. The same trend is observed in the liquid–liquid extraction of *n*-butanol out of water using those ILs [10,31]. The distribution coefficients of *n*-butanol between the ILs and water (Eq. (3)) and the selectivities (Eq. (4)) for the extraction are given in Table 1 for an extraction temperature of 25 °C.

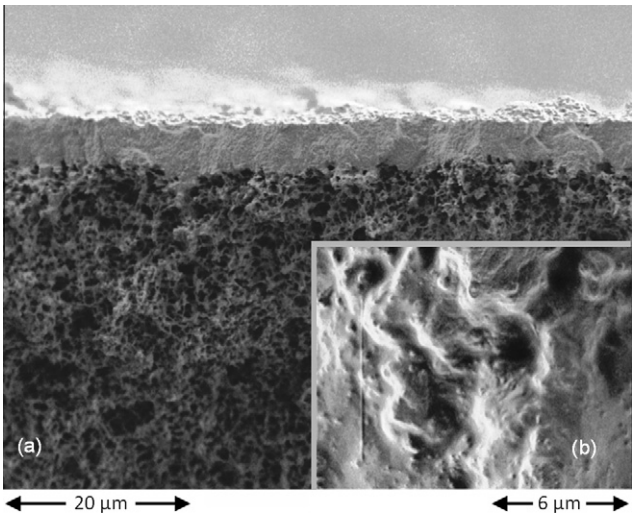

Fig. 4. SEM images: (a) thin silicone film on a porous PP membrane, (b) porous membrane (PP) filled with IL.

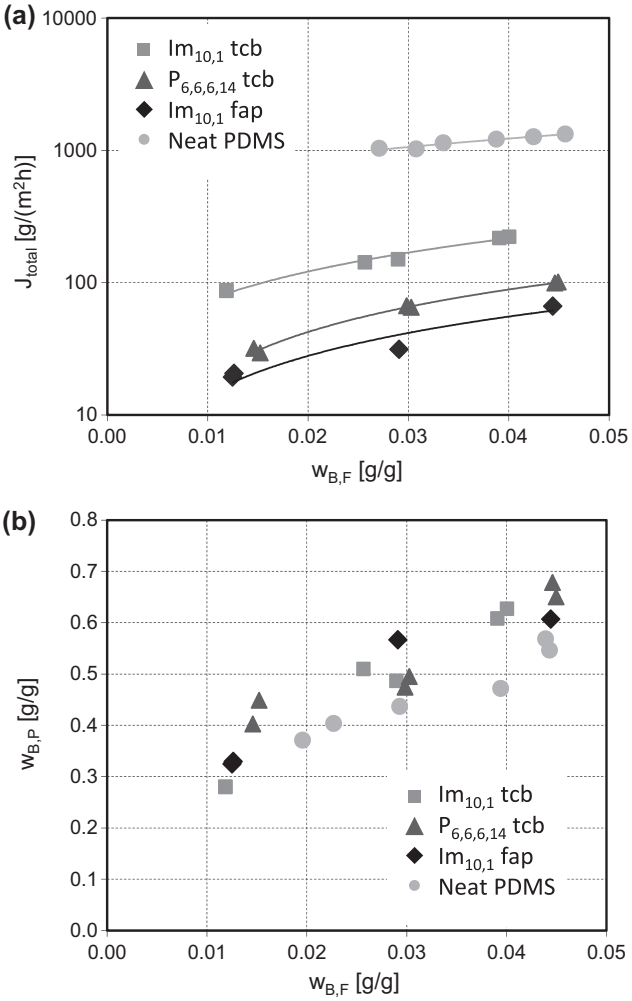

Fig. 5. Pervaporation using IL membranes, containing different ILs, included by silicone layers: (a) permeate fluxes, (b) mass fraction of *n*-butanol in the permeate.

$$D_B = w_{B,IL}/w_{B,aq} \quad (3)$$

$$S_{B,W} = D_B/D_W \quad (4)$$

The comparison of the pervaporation and extraction performances suggests that the permeability of *n*-butanol increases with increasing solubility of *n*-butanol in the IL. Similar results were

Table 1
Differences in distribution coefficients and selectivities for *n*-butanol extraction out of aqueous media using different ILs (25 °C, initial feed concentration of *n*-butanol: 1 wt.%, feed to IL ratio: 1:1, extraction time: 24 h).

IL	D_B [−]	$S_{B,W}$ [−]	
$Im_{10,1}$ tcb	3.2	100	[31]
$P_{6,6,6,14}$ tcb	2.0	500	[10]
$Im_{8,1}$ fap[1]	0.8	420	[31]

[1] Data for $Im_{8,1}$ fap are given, as data for $Im_{10,1}$ fap were currently not available.

reported by Hernández-Fernández et al. for the separation of substrates and products from a transesterification reaction [32]. Moreover, analogous permeation behaviour has been demonstrated for conventional polymer membranes, for which the permeate flux is strongly related to the swelling behaviour of the polymer in the presence of the component to be separated. The permeation properties depend on the affinity of the membrane material for the specific component [33]. Compared to the results of Izák et al., the organic permeate fluxes of our membranes containing $Im_{10,1}$ tcb are up to nine times higher. This difference is probably due to the thinner IL layer, which was produced using a polymeric support membrane instead of a ceramic hollow fibre. Furthermore, *n*-butanol is much more hydrophobic than 1,3-propanediol, which has been investigated by Izák et al. The higher hydrophobicity results in a higher affinity of silicone and IL for *n*-butanol and therefore results in higher permeate fluxes. However, in the separation of 1,3-propanediol, higher average selectivities were achieved.

The permeate fluxes for neat silicone membranes without IL are presented for different thicknesses in Fig. 6a. The maximum permeate flux for the silicone layer of 5 μm thickness is 1400 g/(m^2 h), with a slightly lower selectivity than that of the IL membranes. In the light of this result, our SILMs are currently not competitive with respect to conventional silicone membranes in hydrophobic pervaporation. The lower fluxes of IL membranes coated with silicone layers arise from the greater membrane thickness. Whereas these membranes consist of two 5-μm-thick silicone layers and a 160-μm-thick porous support membrane filled with IL, the active layer of the neat silicone membrane has a thickness of only 5 μm. However, it has to be taken into account that the flux of *n*-butanol is 5.5 times lower for the membrane containing $Im_{10,1}$ tcb, whereas the membrane thickness is 34 times greater than that of the neat silicone membrane. This divergence reveals the superior mass transfer properties of (ionic) liquids compared to cross-linked polymers and demonstrates the potential of SILMs as substitutes for conventional polymer membranes.

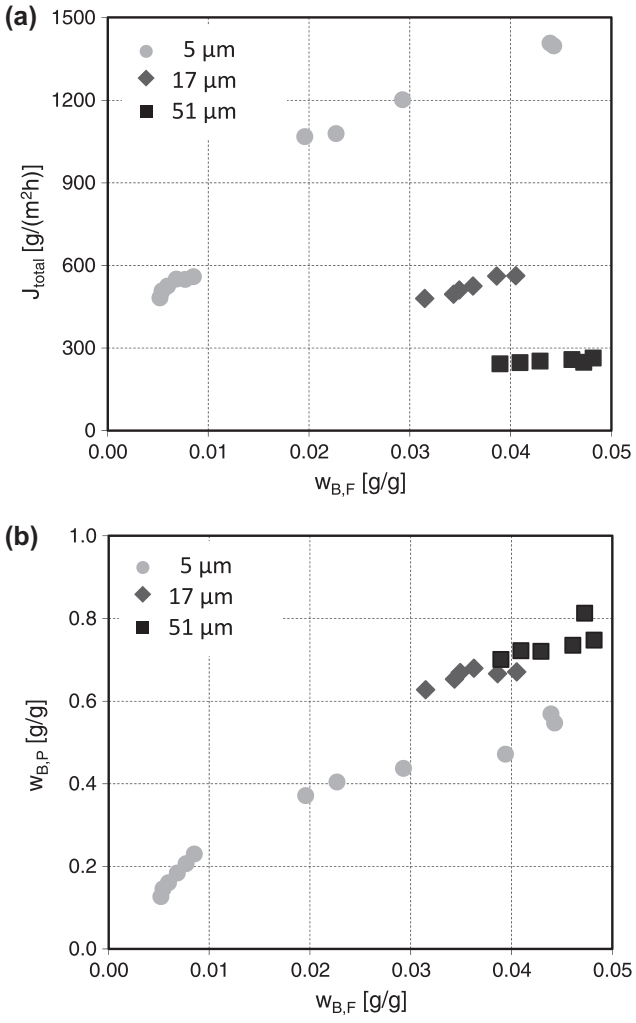

Fig. 6. Influence of the silicone layer thickness on the pervaporation properties of neat silicone membranes: (a) permeate fluxes, (b) mass fraction of *n*-butanol in the permeate.

In contrast to the permeate fluxes, the selectivities of the membranes are not influenced by the ILs (Fig. 5b). The mass fractions of *n*-butanol in the permeate increase with increasing feed concentrations from 30 to 70 wt.%. Because the selectivity for *n*-butanol over water in liquid–liquid extraction increases with increasing hydrophobicity of the ILs [10,31], one would expect that the permeate mass fraction of *n*-butanol is higher for membranes containing $Im_{10,1}$ fap or $P_{6,6,6,14}$ tcb than for the $Im_{10,1}$ tcb membrane, because the selectivity in extraction was more than four times higher compared to $Im_{10,1}$ tcb. However, the mass fraction of *n*-butanol in the permeate seems to be independent of the ILs included in the membranes. Keeping in mind that the influence of the ILs on the *n*-butanol permeation can only be observed when the silicone layer is sufficiently thin, one can speculate that the IL selectivity might have an influence on the selectivity of the membrane if very thin coatings are achieved. In this case, the selectivity of the membrane may be tuned by changing the IL properties. With a thinner silicone layer, the selectivity of the silicone membranes decreases, as illustrated in Fig. 6b. Therefore, the selectivity of ionic liquid membranes might decrease until the selectivity of the IL becomes important. In the literature, the production of dense polymer films with a thickness of 0.1 μm, which is 50 times lower than that obtained in this work, is reported to be feasible [34].

The results of this work suggest that the thickness of the silicone coating should be further minimised to improve the permeate fluxes. Additionally, the thickness of the IL layer has to be reduced, which can be performed by choosing a thinner porous support membrane. However, the thickness of the support membrane is limited to a certain range, because the support membrane is responsible for the mechanical stability.

3.2. Dissolution of IL in a PEBA matrix

As alternative to the immobilisation concept described above, ILs were directly incorporated into a polymer matrix. In order to avoid the limitation due to the thickness of the supported IL layer and the additional mass transfer resistance of a coating can be avoided. Because of its good mass transport properties for *n*-butanol, $Im_{10,1}$ tcb was used for the membrane production to achieve high fluxes of *n*-butanol. $Im_{10,1}$ tcb and silicone are immiscible, yielding in a two-phase solid polymer with liquid inclusions even at concentrations as low as 5 wt.% of IL. In addition to silicone or PDMS, PEBA is often reported to be a suitable polymer for the pervaporation of organic compounds [35]. Due to its increased hydrophilicity relative to silicone, $Im_{10,1}$ tcb shows better solubility in PEBA. It is possible to dissolve up to 55 wt.% of $Im_{10,1}$ tcb in PEBA, forming a single-phase polymer, resistant to moderate mechanical stresses such as tension or pressure.

Fig. 7a shows the permeate flux of a neat PEBA membrane and of PEBA-IL membranes containing 9, 21, 33 and 50 wt.% IL. The permeate flux for the neat PEBA membrane is approximately 200 g/(m^2 h) and is nearly as high as for the membranes, in which ILs were immobilised by the silicone coating. An increase in the IL content of the polymer matrix up to 33 wt.% increases the fluxes up

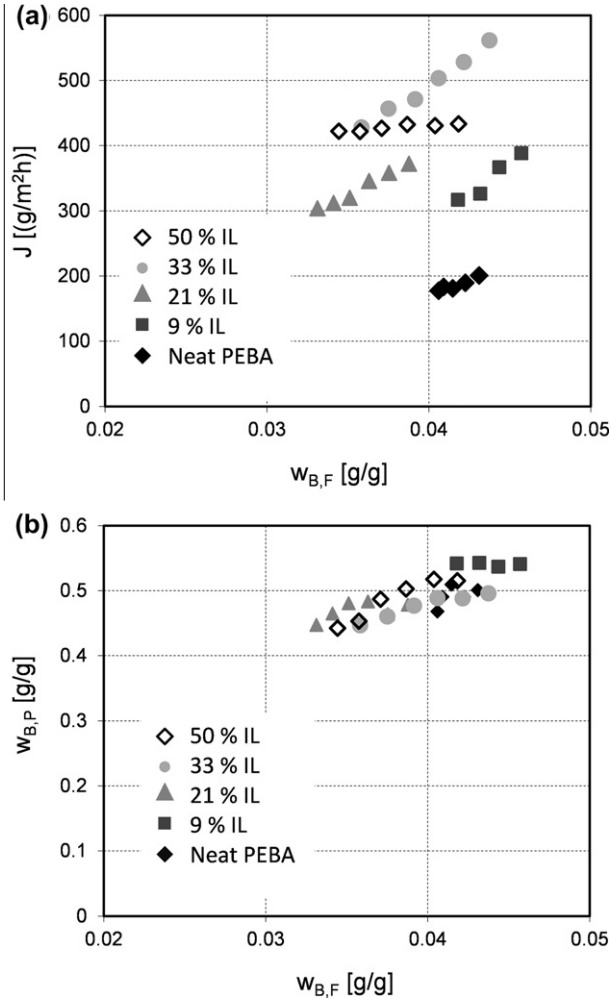

Fig. 7. Pervaporation using IL membranes containing $Im_{10,1}$ tcb included in PEBA: (a) permeate fluxes, (b) mass fraction of *n*-butanol in the permeate.

to 550 g/(m^2 h). Assuming that the immobilised IL has a plasticising effect on the PEBA matrix, this result is consistent with the fact that membrane performances can be improved by increasing the plasticiser concentration in a membrane [36]. The cross sections of the membranes presented in Fig. 8a and b indicate that a high IL content leads to a smoother membrane appearance, resulting from the plasticising properties of the ILs. The membrane

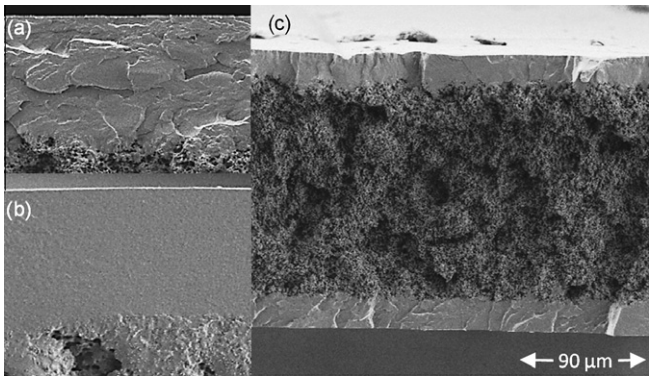

Fig. 8. SEM images: (a) PEBA-IL membrane containing 9 wt.% IL, (b) PEBA-IL membrane containing 50 wt.% IL, (c) porous PP membrane with double-sided PEBA-IL coating, containing 21 wt.% IL.

containing 50 wt.% $Im_{10,1}$ tcb shows slightly lower fluxes compared to the membrane containing 33 wt.% IL. The decreased fluxes observed result from the greater thickness of the PEBA-IL layer containing 50 wt.% of IL as the coating was slightly thicker than for the other membranes. Another possible explanation is that the lowered fluxes compared to the membrane containing 33 wt.% of IL possibly arise from the higher IL concentration. Several studies on ion transport through membranes reported about an optimum plasticiser concentration at which a maximum ion flux occurs [37,38]. Probably a similar effect or the combination of both influences was observed during our experiments. In future investigations this mass transfer behaviour should be addressed further by measurements using different ILs and by using membranes having exactly equal thicknesses.

In contrast to the permeate fluxes, the permeate mass fractions of *n*-butanol show no dependence on the IL content in the membranes and are similar to those for the neat PEBA membranes (Fig. 7b). The determination of the membrane selectivity by the polymer used for immobilisation is also observed, when ILs are included using silicone layers. Although the membrane morphologies and therefore the mass transfer resistances for both immobilisation concepts are fundamentally different, the selectivity is dominated by the polymer material used for immobilisation. No influence of the amount of immobilised IL on the membrane selectivity can be seen. This finding is contradictory to the results of Kohoutová et al. who examined the effect of the IL amount in SILMs on flux and selectivity [28]. They found that an increasing content of benzyl-3-butylimidazolium tetrafluoroborate immobilised in silicone results in an increased selectivity but does not affect the permeate fluxes. The maximum *n*-butanol permeate flux of our membranes containing $Im_{10,1}$ tcb included in PEBA is 275 g/(m^2 h) for a feed concentration of 4.5 wt.%. Therefore the organic flux is almost 10 times higher compared to the results of Kohoutová et al., who included an IL in PDMS as host polymer [28]. These authors used different ILs and polymers which can explain the discrepancies in the result. Böddeker et al. tested neat PEBA membranes in pervaporation of *n*-butanol. At a temperature of 50 °C the permeate fluxes of *n*-butanol were only slightly higher than permeate fluxes determined in this work at similar *n*-butanol concentration in the permeate [35].

For the PEBA-IL membranes, weight losses can be determined after the pervaporation experiments. Those weight losses increase with an increasing IL content of the membrane, indicating a possible loss of IL. The comparison of the weight loss and the mass of IL immobilised in the PEBA-IL layer shows that approximately half of the IL immobilised in the PEBA was leached out of the PEBA-IL membranes during pervaporation. SEM images of the membrane cross sections show that during dip-coating the porous membranes were coated on both sides (Fig. 8c). It can be assumed that the IL on the feed-side coating of the membrane, which was in contact to the feed solution, leached out, whereas the IL in the permeate-side coating was not able to dissolve in the feed medium and remained in the coating. Based on these results, we concluded that the permeate-sided PEBA-IL sufficed to enhance the permeation properties of the membrane with a higher IL content.

In subsequent experiments, membranes with a single layer consisting of IL and PEBA were produced and tested in pervaporation experiments. The decrease in weight of the coating was found to be as large as the mass of IL immobilised in the coating, proving that simple dissolution of $Im_{10,1}$ tcb in PEBA does not yield in a stable SILM, even when the solubility of IL in the feed medium is negligibly small, as it is in case of $Im_{10,1}$ tcb and water. During experiments with single-layered PEBA-IL membranes no changes in flux or selectivity were observed during the experiments although IL leaching occurred. This indicates that leaching of ILs out of the polymer matrix occurs directly when the feed mixture

flows across the membrane. Unfortunately, in literature the stability of liquid membranes is often evaluated by means of steady fluxes and selectivities, membrane weights are often not reported.

To achieve a stable IL immobilisation, only ILs that are totally insoluble in the feed medium should be used for membrane production. Because it is rather unlikely to find ILs with both high solubility for *n*-butanol and insolubility in water, a covalent cross-linking of the ILs is necessary or the contact between the IL and the feed medium must be avoided, e.g., by an additional thin coating on the membrane.

4. Conclusions

It was shown that immobilisation of ILs within membranes influences the permeation properties of pervaporation membranes. The component to be separated should have a high solubility in the IL layer. By choosing a suitable IL, the permeate fluxes could be increased by more than three times relative to a membrane containing a less suitable IL.

The dissolution of $Im_{10,1}$ tcb in PEBA as the host polymer yields in membranes containing up to 50 wt.% IL. For feed concentrations lower than 5 wt.%, these membranes show total permeate fluxes of up to 560 g/(m^2 h) and mass fractions of *n*-butanol in the permeate of 55 wt.%. The permeate fluxes increase with an increasing IL content in the membrane. Because of the leaching of $Im_{10,1}$ tcb from the host polymer an additional polymer coating seems to be necessary for the utilisation of $Im_{10,1}$ tcb in the pervaporation of *n*-butanol.

Although permeate fluxes of SILMs are not competitive to conventional polymer membranes yet, the membranes produced in this work exhibit the advantageous mass transfer properties of SILMs relative to polymer membranes. However, the membrane thickness limits the permeate fluxes for both immobilisation techniques, although the presented permeate fluxes are higher than those of other SILMs reported in the literature.

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